

TITLE**POLYTRIMETHYLENE ETHER GLYCOL WITH EXCELLENT
QUALITY FROM BIOCHEMICALLY-DERIVED 1,3-PROPANEDIOL**

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PRIORITY

This application claims priority from Provisional U.S. Patent Application Serial No. 60/468,228, filed May 6, 2003, incorporated herein by reference.

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FIELD OF THE INVENTION

The present invention involves producing homo- and copolyethers of polytrimethylene ether glycol with excellent quality, in particular the color and the functionality, by use of 1,3-propanediol, preferably obtained from a renewable biological source.

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BACKGROUND OF THE INVENTION

1,3-Propanediol (also hereinafter termed "PDO") is a monomer useful in the production of a variety of polymers including polyesters, polyurethanes, polyethers, and cyclic compounds. Homo and
20 copolyethers of polytrimethylene ether glycol (hereinafter termed "PO3G") are examples of such polymers. The polymers are ultimately used in various applications including fibers, films, etc.

Chemical routes to generate 1,3-propanediol are known. For instance, 1,3-propanediol may be prepared from:

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1. ethylene oxide over a catalyst in the presence of phosphine, water, carbon monoxide, hydrogen and an acid (the "hydroformylation route");
2. the catalytic solution phase hydration of acrolein followed by reduction (the "acrolein route").

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Both of these synthetic routes to 1,3-propanediol involve the intermediate synthesis of 3-hydroxypropionaldehyde (hereinafter also

termed "HPA"). The HPA is reduced to PDO in a final catalytic hydrogenation step. Subsequent final purification involves several processes, including vacuum distillation.

Biochemical routes to 1,3-propanediol have been described that
5 utilize feedstocks produced from biological and renewable resources such as corn feed stock. Such PDO is hereinafter referred to as "biochemical PDO". For example, bacterial strains able to convert glycerol into 1,3-propanediol are found in e.g., in the species *Klebsiella*, *Citrobacter*, *Clostridium*, and *Lactobacillus*. The technique is disclosed in several
10 patents, including, US Patents 5,633,362, 5,686,276, and, most recently, 5,821,092, all of which are incorporated herein by reference. In US Patent 5,821,092, Nagarajan et al., disclose inter alia, a process for the biological production of 1,3-propanediol from glycerol using recombinant organisms. The process incorporates *E. coli* bacteria, transformed with a heterologous
15 pdu diol dehydratase gene, having specificity for 1,2-propanediol. The transformed *E. coli* is grown in the presence of glycerol as a carbon source and 1,3-propanediol is isolated from the growth media. Since both bacteria and yeasts can convert glucose (e.g., corn sugar) or other carbohydrates to glycerol, the process of the invention provided a rapid,
20 inexpensive and environmentally responsible source of 1,3-propanediol monomer useful in the production of polyesters, polyethers, and other polymers.

Precipitations (e.g., with 1,2-propylene glycol, as well as carboxylates or other materials) have been used since the early 1980's to
25 separate the colored and odiferous components from desired products (such as enzymes) to obtain purified preparations. Precipitating the high molecular weight constituents from the fermentor liquors, then bleaching these components with a reducing agent (DE3917645) is known. Alternately, microfiltration followed by nanofiltration to remove the residual
30 compounds has also been found helpful (EP657529) where substances with a high molecular weight above the size of separation are held back.

However, nanofiltration membranes become clogged quickly and can be quite expensive.

Various treatment methods are disclosed in the prior art to remove color precursors present in the PDO, however, the methods are laborious, expensive and increase the cost of the polymer. For instance, Kelsey, US Patent 5,527,973, discloses a process for providing a purified 1,3-propanediol that can be used as a starting material for low color polyester. That process has several disadvantages including the use of large equipment and the need for dilution with large quantities of water, which are difficult to remove from the product. Sunkara et al., US Patent 6,235,948, discloses a process for the removal of color-forming impurities from 1,3-propanediol by a preheating, preferably with heterogeneous acid catalysts such as perfluorinated ion exchange polymers. The catalyst is filtered off, and the 1,3-propanediol is then isolated, preferably by vacuum distillation. Preparation of polytrimethylene ether glycol from purified diol gave APHA values of 30 – 40, however, the molecular weight of the polymers were not reported.

The polyalkylene ether glycols are generally prepared by the acid-catalyzed elimination of water from the corresponding alkylene glycol or the acid-catalyzed ring opening of the alkylene oxide. For example, polytrimethylene ether glycol can be prepared by dehydration of 1,3-propanediol or by ring opening polymerization of oxetane using soluble acid catalysts. Methods for making PO3G from the glycol, using sulfuric acid catalyst, are fully described in U.S. Patent Application publication Nos. 2002/0007043A1 and 2002/0010374A1, all of which are incorporated herein by reference. The polyether glycol prepared by the process is purified by the methods known in the art. The purification process for polytrimethylene ether glycol typically comprises (1) a hydrolysis step to hydrolyze the acid esters formed during the polymerization (2) water extraction steps to remove the acid catalyst, unreacted monomer, low molecular weight linear oligomers and oligomers of cyclic ethers, (3) a base treatment, typically with a slurry of calcium hydroxide, to neutralize

and precipitate the residual acid present, and (4) drying and filtration of the polymer to remove the residual water and solids.

It is well known that the polytrimethylene ether glycol produced from the acid catalyzed polycondensation of 1,3-propanediol has quality problems, in particular, the color is not acceptable to the industry. The polymer quality is in general dependent on the quality of the raw material, PDO. Besides the raw material, the polymerization process conditions and stability of the polymer are also responsible for discoloration to some extent. Particularly in the case of polytrimethylene ether glycol, the polyether diols tend to have light color, a property that is undesirable in many end-uses. The polytrimethylene ether glycols are easily discolored by contact with oxygen or air, particularly at elevated temperatures, so the polymerization is effected under a nitrogen atmosphere and the polyether diols are stored in the presence of inert gas. As an additional precaution, a small concentration of a suitable antioxidant is added. Preferred is butylated hydroxytoluene (BHT, 2,6-di-t-butyl-4-methylphenol) at a concentration of about 100-500 microg/g (micrograms/gram) polyether.

Also, attempts have been made to reduce the color of polytrimethylene ether glycols by conventional means without much success. For instance, Morris et al., US Patent 2,520,733, notes the peculiar discoloration tendency for the polytrimethylene ether glycol from the polymerization of PDO in the presence of acid catalyst. The many methods they tried that failed to improve the color of polytrimethylene glycols included the use of activated carbons, activated aluminas, silica gels, percolation alone, and hydrogenation alone. Consequently, they developed a process for the purification of polyols prepared from 1,3-propanediol in the presence of acid catalyst (2.5 to 6% by weight) and at a temperature from about 175°C to 200°C. This purification process involves percolation of the polymer through Fuller's earth followed by hydrogenation. This extensive purification process gave a final product that was light yellow in color, in fact, this procedure yielded polytrimethylene ether glycol (Example XI therein) for which the color was

only reduced to an 8 Gardner color, a quality corresponding to an APHA value of >300 and totally inadequate for current requirements.

5 Mason in US Patent 3,326,985 discloses a procedure for the preparation of polytrimethylene ether glycol of molecular weights in the range of 1200-1400 possessing improved color by vacuum stripping, under nitrogen, polytrimethylene ether glycol of lower molecular weight. The color levels, however, are not quantified and would not have approached the above requirement.

10 SUMMARY OF THE INVENTION

 A process is disclosed comprising contacting 1,3-propanediol with a suitable polymerization catalyst to produce polytrimethylene ether glycol, wherein the 1,3-propanediol, before contact, comprises about 10 microg/g [micrograms per gram] or less of peroxide compounds based on the weight of the 1,3-propanediol. Preferably, the 1,3-propanediol comprises about 100 microg/g or less of carbonyl compounds based on the weight of the PDO. Also, preferably, the 1,3-propanediol comprises about 100 microg/g or less of monofunctional alcohol compounds based on the weight of the PDO.

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DETAILED DESCRIPTION OF THE INVENTION

 Unless stated otherwise, all percentages, parts, ratios, etc., are by weight. Trademarks are shown in upper case.

 Further, when an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed.

30 This invention is directed to the production of an excellent quality of polytrimethylene ether glycol from the (acid) catalyzed polycondensation of 1,3-propanediol. The present inventors have found that to date the quality

of the 1,3-propanediol manufactured from the petrochemical routes is not good enough to produce high quality PO3G polymers. This is due to the presence of impurities such as carbonyl compounds, e.g., hydroxypropionaldehyde, peroxide-forming compounds of uncertain structure, monofunctional alcohols (such as 2-hydroxyethyl-1,3-dioxane, hereinafter "HED"), and acidic compounds detectable by pH measurements. The monofunctional alcohols act as chain terminating agents during polymerization, they can be incorporated into the polymer as "dead ends" that can affect the polymer functionality. Monofunctional alcohols may or may not contribute to color formation. However, in general, the carbonyl compounds frequently are associated with color bodies, one could expect that the greater the carbonyl number, the darker will be the color. Some of the above impurities in the PDO can generate color during the acid catalyzed polymerization process.

In accordance with a first aspect, the present invention comprises contacting 1,3-propanediol with a suitable polymerization catalyst to produce polytrimethylene ether glycol, wherein the 1,3-propanediol, before contact, comprises about 10 microg/g or less peroxide compounds, based on the weight of the 1,3-propanediol. In general, alkenes, ethers, and allylic species are prone to peroxide formation and the formed peroxides can be determined by use of commercially available test strips or by iodometric titration in a manner known in the art.

In accordance with another aspect of the present invention, the 1,3-propanediol further comprises about 100 microg/g or less carbonyl compounds based on the weight of the PDO. Preferably, the PDO comprises about 75 microg/g or less, more preferably about 50 microg/g or less, most preferably about 25 microg/g or less carbonyl compounds based on the weight of the PDO. Illustrative examples of carbonyl compounds are hydroxypropionaldehyde and aldehydes present in an acetal form, such as acetals from the reaction 3-hydroxypropionaldehyde and 1,3-propanediol. The carbonyl content is determined by UV detection

after conversion of the carbonyl compounds into the dinitrophenylhydrazones in a manner well known in the art.

In accordance with another aspect of the present invention, the 1,3-propanediol further comprises about 100 microg/g or less monofunctional alcohol compounds based on the weight of the PDO. Preferably, the PDO comprises about 75 microg/g or less, more preferably about 50 microg/g or less, most preferably about 25 microg/g or less monofunctional alcohol compounds based on the weight of the PDO. Illustrative examples of a monofunctional alcohol compounds are HED and 3-hydroxytetrahydropyran.

In accordance with another aspect of the present invention, the 1,3-propanediol contains at least 99.95% by weight of said diols, i.e., it is at least 99.95% pure.

In accordance with another aspect of the present invention, a blend of the 1,3-propanediol with an equal weight of distilled water has a pH ("50/50 pH") between 6.0 and 7.5, preferably between 6.0 and 7.0.

In accordance with another aspect, the present invention provides a process comprising contacting a biochemically-derived 1,3-propanediol with a suitable polymerization catalyst to produce polytrimethylene ether glycol, wherein the 1,3-propanediol has a 50/50 pH of 6.0 – 7.5 and comprises about 100 microg/g or less carbonyl compounds, about 10 microg/g or less peroxide compounds and about 100 microg/g or less monofunctional alcohol compounds based on the weight of the PDO.

The present inventors have found that starting with a raw material containing low amounts of these impurities, particularly those below the limits specified herein, substantially reduces or eliminates altogether the need to post-treat the PDO and PO3G. Preferably, the PDO is biochemical PDO (is biochemically derived). Most preferably, the PDO used in processes in accordance with the present invention is derived from biological and renewable sources as described above, i.e., is prepared from a fermentation process and from corn feed stock.

In accordance with another aspect of the present invention, a composition comprises: biochemically-derived 1,3-propanediol, wherein the 1,3-propanediol comprises about 100 microg/g or less carbonyl compounds, about 10 microg/g or less peroxide compounds and about 5 100 microg/g or less monofunctional alcohol compounds, based on the weight of 1,3-propanediol. According to yet another aspect in accordance with the present invention, polytrimethylene ether glycol is derived from the polymerization of biochemically-derived 1,3-propanediol.

Preferably, the 1,3-propanediol used according to the present 10 invention has a color value of less than about 10 APHA. More preferably, the 1,3-propanediol used according to the present invention has a color value of less than about 5 APHA. The APHA color measurement is described in Test Method 1, below.

A simple procedure provides a quick method to ascertain the PDO 15 quality for PO3G production, without the time-consuming procedure to make the PO3G. The procedure depends on the finding that impurities in the PDO that would cause color formation in the PO3G reveal themselves rapidly under the mild conditions of the accelerated acid heat test (AAHT, Test Method 6). The AAHT procedure involves a short heating period with 20 concentrated sulfuric acid (1% by weight based on the PDO). The heating period is 10 min. at 170°C. Thus, the AAHT procedure converts color precursors to color, but no significant polyether glycol formation occurs. Preferably, the PDO has a color value after AAHT of less than about 15 APHA. More preferably, the PDO has a color value after AAHT of less 25 than about 10 APHA.

The PO3G made from the PDO of the present invention can be PO3G homo- or co-polymer. For example, the PDO can be polymerized with other diols (below) to make co-polymer.

The PDO copolymers useful in the present invention can contain up 30 to 50% by weight (preferably 20% by weight or less) of comonomer diols in addition to the 1,3-propanediol and/or its oligomers. Comonomer diols that are suitable for use in the process include aliphatic diols, for example,

ethylenediol, 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol,
1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol,
3,3,4,4,5,5-hexafluoro-1,5-pentanediol, 2,2,3,3,4,4,5,5-octafluoro-1,6-
hexanediol, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1,12-
5 dodecanediol, cycloaliphatic diols, for example, 1,4-cyclohexanediol,
1,4-cyclohexanedimethanol and isosorbide, polyhydroxy compounds, for
example, glycerol, trimethylolpropane, and pentaerythritol. A preferred
group of comonomer diol is selected from the group consisting of
2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-
10 propanediol, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, 1,6-hexanediol,
1,8-octanediol, 1,10-decanediol, isosorbide, and mixtures thereof. C₆ –
C₁₀ diols are particularly useful. Thermal stabilizers, antioxidants and
coloring materials may be added to the polymerization mixture or to the
final polymer if necessary.

15 In some instances, it may be desirable to use up to 10% or more of
low molecular weight oligomers where they are available. Thus, preferably
the starting material comprises 1,3-propanediol and the dimer and trimer
thereof. The most preferred starting material is comprised of 90% by
weight or more 1,3-propanediol, more preferably 99 weight % or more.

20 Processes for producing PO3G from PDO are generally known in
the art. For example, U.S. Patent No. 2,520,733, which is incorporated
herein by reference, discloses polymers and copolymers of
polytrimethylene ether glycol and a process for preparation of these
polymers from 1,3-propanediol in the presence of a dehydration catalyst
25 such as iodine, inorganic acids (e.g., sulfuric acid) and organic acids.

The polytrimethylene ether diol is, preferably, prepared by an acid-
catalyzed polycondensation of 1,3-propanediol as described in U.S.
Published Patent Application Numbers 2002/7043 A1 and 2002/10374 A1,
both of which are hereby incorporated by reference. The polytrimethylene
30 ether glycol can also be prepared by a ring-opening polymerization of a
cyclic ether, oxetane, as described in J. Polymer Sci., Polymer Chemistry
Ed. 28, 429 – 444 (1985) which is also incorporated by reference. The

polycondensation of 1,3-propanediol is preferred over the use of oxetane. As desired, the polyether glycol prepared by the process of the present invention can be purified further to remove the acid present by means known in the art. It should be recognized that in certain applications the product might be used without further purification. However, the purification process improves the polymer quality and functionality significantly and it is comprised of (1) a hydrolysis step to hydrolyze the acid esters that are formed during the polymerization and (2) typically (a) water extraction steps to remove the acid, unreacted monomer, low molecular weight linear oligomers and oligomers of cyclic ethers, (b) a solid base treatment to neutralize the residual acid present and (c) drying and filtration of the polymer to remove the residual water and solids.

The PO3G made from the PDO of the present invention, preferably, has a color value of less than about 50 APHA. More preferably, the PO3G color value is less than 30 APHA. Preferably, the PO3G products made using the PDO monomer/oligomers of the present invention have a molecular weight of about 250 to about 5000, preferably about 500 to about 4000, and most preferably about 1000 to about 3000.

The process of the present invention will provide polytrimethylene ether glycol with improvements in functionality and polymer color.

MATERIALS and TEST METHODS

Test Method 1. Measurement of APHA Values

A Hunterlab ColorQuest Spectrocolorimeter (Reston, VA) was used to measure the PDO and polymer color. Color numbers are measured as APHA values (Platinum-Cobalt System) according to ASTM D-1209. The polymer molecular weights are calculated from their hydroxyl numbers obtained from titration method.

Test Method 2. Measurement of PDO content & HED (by gas chromatography).

Undiluted PDO samples are injected into a gas chromatograph equipped with a Wax (e.g., Phenomenex Zorbax Wax, DB-Wax, HP Innowax, or equivalent) capillary column and flame ionization detector (FID). The FID produces a signal proportional to the concentration of the analyte as a function of time, and the signal is acquired on an integrator or stored as x,y data in a computer. Each component separated and detected is seen as a "peak" when the signal is plotted vs. time. All impurities are assumed to have the same wt-% response factor on the FID as PDO. The % purity is calculated as area %. Lower detection limit: 5 microg/g.

Test Method 3. Measurement of carbonyl content (by spectrophotometric analysis).

Carbonyl compounds are converted to the dinitrophenylhydrazone derivatives prior to spectrophotometric quantification. Lower detection limit: 2 microg/g.

Test Method 4. Measurement of peroxide content

The peroxides in PDO were determined using either commercially available Peroxide Test Strips, 0.5-25 microg/g EM Quant® or iodometric titration method. The titration method involves by adding a 5 g of sample to 50 ml of 2-propanol/acetic acid solution and then by titrating the solution with 0.01N sodium thiosulfate solution. The lower detection limit is 0.5 microg/g. When using test strips, concentrations greater than 25 microg/g can be quantified by dilution of samples to the 5 – 25 microg/g range or the use of test strips designed for higher concentrations.

Test Method 5. Measurement of pH (pH shows the level of acidic impurities on a logarithmic scale).

A 50:50 blend of PDO and distilled water was used to measure the pH of the solution using a pH meter.

Test Method 6. AAHT Procedure.

PDO (150 g) and 1.5 g of concentrated sulfuric acid were charged to a 250-mL three-neck flask. The solution was stirred mechanically and then heated to 170°C for 10 min. under nitrogen atmosphere. After 10 min., the solution was cooled to room temperature and the color was measured according to Test Method 1.

EXAMPLES10 Examples 1 – 3

1,3-propanediol is available commercially from two petrochemical routes. DuPont manufactures 1,3-propanediol starting from acrolein; PDO is also available from ethylene oxide sources. DuPont is also making 1,3-propanediol using glucose derived from corn as a renewable source.

15 Samples of PDOs from each synthesis route were analyzed for PDO content, 2-hydroxethyl-1,3-dioxane (HED) content, carbonyl content, peroxide content and acidity value as described in Methods above. The results are shown in Table 1. APHA values were determined on the PDO before and after the AAHT procedure and the results are shown in

20 Table 2.

Table 1: Chemical Analysis on 1,3-propanediol

Examp le	Feed Source for PDO	PDO Purity %	HED microg/g	Carbonyl s microg/g	Peroxide s microg/g	pH 50/5 0
1	Corn	99.997	ND*	ND*	ND*	6.82
2	Acrolein	99.968	80	93	56	4.87
3	Ethylene oxide	99.917	310	198	ND*	5.88

*ND not detectable (see Test Methods for limits)

The results in Table 1 indicate the PDO originating from the biochemical route has highest purity and contains least impurities versus PDO derived from petrochemical sources.

- 5 Table 2. Discoloration of 1,3-propanediol with acid treatment at 170°C for 10 min.

Example	Feed source for PDO	PDO color (APHA) before AAHT	PDO color (APHA) after AAHT
1	Corn	3	8
2	Acrolein	3	50
3	Ethylene oxide	4	14

- Table 2 shows that the PDO in Example 1 discolors least after the AAHT test suggesting that there are no color precursor impurities. The purity of the acrolein-based 1,3-propanediol is higher and contains less carbonyl compounds than ethylene oxide-based diol (as shown in Table 1). However, the acrolein based-diol discolored more strongly in the AAHT process indicating the presence of relatively high concentration of color precursor impurities. Also, this PDO contains peroxide-forming compounds as evident from the presence of peroxides.

Example 4 Preparation of PO3G from biochemical-PDO.

The 1,3-propanediol obtained from the biochemical route is used to make polymer as described below:

- 20 A 22-L, 4-necked, round-bottomed flask, equipped with a nitrogen inlet, and a distillation head was charged with 8392 g of 1,3-propanediol. The liquid was sparged with nitrogen at a rate of 10 L/min. and mechanical stirring (using a stirring magnet driven by a magnetic stirrer below the flask) was done for about 15 min. After 15 min., 76.35 grams of sulfuric acid was slowly added drop-wise from a separatory funnel through one of

the ports over a period of at least 5 minutes. When this was finished, 15 g of PDO was added to the separatory funnel and swirled to remove any residual sulfuric acid. This was added to the flask. The mixture was stirred and sparged as above and heated to 160°C. The water of reaction
5 was removed by distillation and was collected continuously during the polymerization reaction. The reaction was continued for 38.5 hours, after which it was allowed to cool (while stirring and sparging were maintained) to 45°C. The crude polymer obtained has a number average molecular weight of 2130 as determined by NMR and an APHA color of 59.

10 The crude material was hydrolyzed as follows. The crude polymer was added to a 22-L, 5-necked, round-bottom flask, (equipped with a condenser and a mechanical mixer) along with an equal volume of distilled water. This mixture was stirred mechanically, sparged with nitrogen at a rate of about 150 mL/min. and heated to 100°C. It was allowed to reflux
15 for 4 hours after which the heat was turned off and the mixture allowed to cool to 45°C. The stirring was discontinued and the sparging reduced to a minimum. Phase separation occurred during cooling. The aqueous phase water was removed and discarded. A volume of distilled water equal to the initial amount was added to the wet polymer remaining in the flask.
20 Mixing, sparging and heating to 100°C was done again for 1 hour after which the heat was turned off and the material allowed to cool as before. The aqueous phase was removed and discarded.

The residual sulphuric acid was determined by titration and neutralized with an excess of calcium hydroxide. The polymer was dried
25 under reduced pressure at 90°C for 3 hours and then filtered through a Whatman filter paper precoated with a CELPURE C-65 filter aid. The purified polymer obtained has a number average molecular weight of 2229 as determined by NMR and an APHA color of 32.

30 Example 5 Preparation of PO3G from 1,3-propanediol.

The polymer is prepared as described in Example 4, except the 1,3-propanediol used is derived from an acrolein route.

Example 6 Preparation of PO3G from 1,3-propanediol.

The polymer is prepared as described in Example 4, except the 1,3-propanediol used is derived from an ethylene oxide route.

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Table 3: PO3G polymer color

Example	Feed Source for PDO	Crude Polymer		Purified Polymer	
		Mn	Color (APHA)	Mn	Color (APHA)
4	Corn	2130	59	2229	32
5	Acrolein	2256	185	2341	157
6	Ethylene oxide	2157	102	2170	109

Table 3 shows that the purified PO3G derived from the PDO of Example 1 has the lowest color than the polymers derived from other PDOs.